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(54) Name of the Invention: Fiber Reinforced Plastic Sheet, Reinforcement Method for Civil Construction Materials and Civil Construction Buildings

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## DETAILED DESCRIPTION

### 1. NAME OF THE INVENTION

Fiber Reinforced Plastic Sheet, Reinforcement Method for Civil Construction Materials and Civil Construction Buildings

### 2. SCOPE OF CLAIMS OF THE PATENT APPLICATION

- (1) A fiber reinforced plastic sheet that is characterized by forming and hardening of a compound containing a polymerizing monomer-bridging heat-hardening resin which consists of at least one polymer with a double bonding value of 750 ~ 2600 to be bridged and a polymerizing monomer for bridging containing 20 ~ 40 weight % of the polymerizing monomer for bridging, and
  - (b) a fiber reinforcement material with the ratio of ingredients (a) and (b) being 75 ~ 98 weight % ingredient (a) and 2 ~ 25 weight % ingredient (b).
- (2) A fiber reinforced plastic sheet in accordance with claim 1, that is made into sheets with a thickness of 0.4 ~ 1.8 mm.
  - (3) A civil construction material characterized by the use of fiber reinforced plastic sheet as described in claim 1 or claim 2.
  - (4) A reinforcement process for civil construction buildings employing the use of the civil construction material as described in Claim 3.

### 3. DETAILED EXPLANATION OF THE INVENTION

#### Field of Industrial Application

This invention concerns a fiber reinforced plastic sheet, reinforced civil construction materials, and a method of reinforcement using the said materials for civil construction buildings with superior fit to the part to be covered that is useful in the reinforcement of civil construction materials such as concrete and metal.

#### Conventional Technology

Regarding the covering method of concrete buildings and metal structures, rubber linings, resin linings, other organic material coatings or inorganic material coatings are used. As resin linings with a wide variety of uses, the following are available:

- (1) PRP lining method with liquid resin that hardens at normal temperatures

This is a method in which a fiber glass base material is soaked and lined in layers with a liquid resin compound which is created by dissolving unsaturated polyester with a vinyl monomer such as styrene and using a normal temperature hydrolytic peroxide such as methyl ethyl ketone peroxide (MEKPO) as a hardener, or a compound which is created by dissolving epoxy (meta) acrylate resin (vinyl ester resin) with a vinyl monomer such as styrene and using MEKPO as a hardener, or a liquid resin compound which consists of a liquid epoxy resin with an amine type normal temperature hardener such as Grade 1 amine or Grade 3 amine which is then hardened at normal temperatures.

Because this method is comprised of a resin that hardens at normal temperatures, there are problems for the lining material, such as the time period for application being short, the work environment becoming poor due to monomer formation, and stability of the quality due to uneven blending during measuring and mixing, and lamination by manual coating performed on site.

## (2) Coating lining method with liquid resin

Some of the liquid resin lining methods are: A coating method in which a liquid resin such as unsaturated polyester resin, vinyl ester resin, epoxy resin, urethane resin of the normal temperature hardening type described above are brushed on or sprayed on, or a coating method in which a liquid resin compound consisting of unsaturated polyester, vinyl ester resin, a resin that hardens under ultraviolet irradiation such as urethane acrylate blended with vinyl monomer and a light sensitizer, unsaturated polyester, and coloring are brushed on or sprayed on and then allowed to harden using an ultraviolet irradiator. However, these methods provide a thin film coating of approximately 10 ~ 200  $\mu$  and have disadvantages such as poor durability for a long period of time and poor impact resistance against external force. Another disadvantage is that it is also extremely difficult to provide a thick coating for long-term durability.

## (3) Lining method by lining with heat-hardening "prepreg" sheet

A "prepreg" sheet in the solid or semi-solid state, prepared by soaking a fiber base material in a liquid compound consisting of solid or semi-solid unsaturated polyester, vinyl ester resin, epoxy resin with a diluent, a heat activated latent hardener, and a solvent, etc., each in the appropriate amount, which is then dried and the solvent removed, or a cured "prepreg" sheet in the solid state (generally called "SMC") which is prepared by soaking a fiber base material in a liquid compound consisting of an unsaturated polyester resin or vinyl ester resin partially containing COOH radicals on the end or in the side chain, MgO, and a filler such as organic peroxide and calcium carbonate

that are heat activated, which is then hardened by using hot air, infrared light, or a heat board.

However, such heat hardened "preleg" sheets are difficult to apply to larger tanks, pipes or structures with large heat capacity because the hardening process did not progress without heating. The "preleg" sheets are also impractical for storing, because they will gradually harden at normal temperatures if left for a long period of time.

#### Problems this Invention Attempts to Solve

In patent application publications, the lining process methods such as described in patent application 1986-15881 and patent application 1985-50581 are shown to improve the above lining methods by preparing a sheet-shaped formative material in advance, bonding it onto the structural material under pressure, then hardening it with ultraviolet or infrared rays. Because these sheets are solid, they are easy to handle. Also, they are excellent methods since the sheets are produced under controlled conditions at plants, etc. to provide an even thickness of the lining layer.

However, the light hardening methods have the following disadvantages. (1) When a charging material or a reinforcer such as flakes are mixed in, the resin carrier tends to remain unhardened. (2) Mercury lamps and other light sources are used, but it is difficult to evenly irradiate pipes and other irregular shapes which results in uneven hardening, and the lining may peel off due to uneven hardening. (3) It is difficult to control storage, since the lining hardens under natural sun light. In order to solve these problems, the inventor of this invention focused on a method to line fiber reinforced resin hardened materials (FRP) that have completed hardening. However, the distortion flexure is small in the generally known thin FRP sheets and it is difficult to apply it in variably curved areas.

Also, when using the soft resins that are commonly used in this industry, they have disadvantages such as the expansion rate not becoming smaller as time passes. Furthermore, other problems are the significant lack of flexibility at low temperatures and the significant lack of fit to the body to be covered during or after installation in winter.

#### Methods for Resolving the Problems

The inventor has achieved this invention as a result of studying and reviewing the methods in order

to alleviate the disadvantages of installation etc. in the current state, without losing the basic properties of FRP. That is, to provide a fiber reinforced plastic sheet, civil construction materials that use the said plastic sheet as reinforcer, and a reinforcement method for civil construction buildings using the said sheet or materials, where the fiber reinforced plastic sheet is characterized by formation and hardening of the compound with preferably a thickness of 0.4 ~ 1.8 mm, containing ingredient (a), a polymerizing monomer-bridging heat-hardening resin containing at least a polymer with a double bond value of 750 ~ 2600 to be bridged, a polymerizing monomer for bridging and containing 20 ~ 40 weight % of the polymerizing monomer for bridging, and ingredient (b), a fiber reinforcement material with the ratio of ingredients (a) and (b) being 75 ~ 98 weight % ingredient (a) and 2 ~ 25 weight % ingredient (b).

Some of the polymerizing monomer-bridging heat-hardening resin compounds in this invention are unsaturated polyesters, vinyl ester resins, etc. containing a small amount of polymerizing monomer for bridging, and the others that are preferably used contain hardening agents, hardening accelerators, and other additives.

The polymerizing monomer-bridging heat-hardening unsaturated polyester resin compounds that consist of unsaturated polyester and polymerizing monomer for bridging are manufactured by condensation polymerization of the glycol series with  $\alpha$ -,  $\beta$ -unsaturated dibasic acid or its acidic anhydride, an aromatic saturated dibasic acid or its anhydride. In some cases, they are manufactured by dissolving the 60 ~ 75 weight part of the unsaturated polyester made also with the aliphatic series or the aliphatic chain series saturated dibasic acid as the acid ingredient, in the 25 ~ 40 weight part of the  $\alpha$ -,  $\beta$ -unsaturated monomer. Further, the polymerizing monomer-bridging heat-hardening vinyl ester resin compounds are the following: Unsaturated polyester with vinyl-modified ends, and the epoxy resin structure (epoxy resin) with vinyl-modified ends with a blend of polymerizing monomer for bridging, at least, as described above. In this case, flexibility is required for the hardened material. As the means to provide flexibility, for example, a method to denature the ends of the epoxy resin with a polybutadiene polymer or butadiene acrylonitrile nonpolymer is used.

For these, a hardening catalyst and hardening accelerator are used as needed, and further, a viscosity agent, filler, low shrinkage agent, etc. are added. However, the addition of a hardening catalyst and hardening accelerator is particularly desirable, since they promote the hardening reaction.

Regarding the  $\alpha$ -,  $\beta$ -unsaturated dibasic acid or its acidic anhydride noted above, maleic acid,

fumaric acid, itaconic acid, citraconic acid, chlormaleic acid, and their esters are available. Regarding the aromatic saturated dibasic acid or its anhydride, phthalic acid, anhydrous phthalic acid, isophthalic acid, terephthalic acid, nitrophthalic acid, tetrahydroanhydrous phthalic acid, endomethylene tetrahydroanhydrous phthalic acid, halogenized anhydrous phthalic acid, and their esters are available. Regarding the aliphatic series or the aliphatic chain series saturated dibasic acids, oxalic acid, malonic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, glutaric acid, hexahydroanhydrous phthalic acid, and their esters, that are used singularly or in combination, are available.

Regarding the glycol series, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, 1,3-butanediol, 1,4-butanediol, 2-methyl propane, 1,3-diol, neopentyl glycol, triethylene glycol, 1,5-pentanediol, 1,6-hexanediol, bisphenol A, bisphenol hydride A, ethylene glycol carbonate, 2,2- --- di --- (4-hydroxy-proboxy-diphenyl) propane, that are used singularly or in combination, are available. In addition, as a part of the glycol series and acid ingredients, condensation polymerization products such as polyethylene terephthalate may be used.

Furthermore, either an amine monomer such as the above noted glycol monomers or ethylene diamine, carbon, monomethyl diethanol amine, monoethyl diethanol amine to which an alkylene oxide, e.g., ethylene oxide, propylene oxide, butylene oxide, styrene oxide, is added singularly, or the co-polymers or the polyether polyol series which consists of a mixture of those co-polymers may be used. The average molecular weight is preferably 500 ~ 10000. In addition, regarding polyester polyol, the condensation product of polybasic acid and polyvalent alcohol is used. For example, polyester polyol having an end OH-base obtained by reacting a single acid or a mixture of maleic acid, fumaric acid, adipic acid, or phthalic acid with ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol can be used. The average molecular weight is preferably 500 ~ 10000. Preferably used are the polyether polyol series in the liquid state at normal temperatures which are easy to handle.

The amount of the  $\alpha$ -,  $\beta$ -unsaturated dibasic acid or their acidic anhydride that is mixed in the unsaturated polyester used in this invention plays an extremely important role. As a scale for indicating the amount to be mixed, the following double bond titer is used:

Double bond titer = (amount of polymer to be bridged) / (No. of mols for the unsaturated dibasic acid)

Here, the more unsaturated dibasic acid is used, the smaller is the value of the double bond titer and

the higher is the <sup>crossing</sup>bridging density after hardening, allowing the material to become hardened. If only a small amount of unsaturated dibasic acid is used, then the opposite tends to be the case.

In this invention, the appropriate double bond titer for the polymer to be bridged is 750 ~ 2600.

Figure 1 shows the relationship between the double bond titer and the tensile expansion rate for unsaturated polyester. Figure 2 shows the relationship between the double bond titer and the dimension of the inner diameter break when bent (the cross-section bending fixture is clamped to the sample and the inner diameter of the fixture where the break occurs is recorded). From these figures, when the double bond titer is less than 750, flexibility is significantly reduced. When the double bond titer is greater than 2600, flexibility tends to be stable, and further, when water resistance, thermal water resistance, etc. are taken into consideration, a double bond titer beyond this would be unnecessary. In Figures 1 and 2, the polymer to be bridged was unsaturated polyester, the polymerizing monomer for bridging was styrene, the ratio of the polymer to the monomer was 70:30. In 100 weight parts of this compound, 6% naphthenic acid cobalt was 0.4 weight part and MEKPO (methyl ethyl ketone peroxide) was 1.0 weight part, and sheet of 1.00 mm thickness were created and from this sheet, a JIS-K-6301 No. 1 dumbbell was collected and measured at 23°C.

As  $\alpha$ -,  $\beta$ -unsaturated monomers for the polymerizing monomer for bridging used in this invention may be listed the vinyl compounds such as styrene, vinyl toluene,  $\alpha$ -methylstyrene, chlorstyrene, dichlorstyrene, vinyl naphthene, ethylvinylethyl, methylvinylketone, methylacrylate, ethylacrylate, methylmetacrylate, acrylonitril, metacrilonitril, and aryl compounds such as diarylphthalate, diarylfumarate, diarylsuccinate, triarylcyanate, and bridgeable vinyl monomer or vinyl oligomer. They may be used singularly or in combination. If they are to be used by themselves, styrene is most preferable.

The content of the monomer (for example, styrene) in the polymerizing monomer-bridging heat-hardening resin compound used in this invention greatly affects the properties of the sheet. In particular, when styrene is used, if its content is increased, there appears a phenomenon in which the hardened section gradually becomes harder as time passes, even if the degree of flexibility at the initial stage was great. Especially, when styrene is over 40%, this phenomenon becomes significant and the problem occurs during use. The cause of this phenomenon is: (1) in case of soft resin, the amount of unsaturated dibasic acid co-polymerized in the unsaturated polyester, e.g., is small as described above. As is known, in the three dimensional bridging mechanism of the hardened material for the polymerizing monomer-bridging heat-hardening unsaturated polyester

resin compound, the double bond of the unsaturated dibasic acid and the monomer are reacting. If the degree of copolymerization of the unsaturated dibasic acid is small, the corresponding relevant amount of the monomer decreases. Therefore, if more than the relevant amount of monomer is contained, the excess monomer remains in an unreacted state. It is believed that these unreacted monomers gradually reacts with each other and harden as time passes.

The results of measurements within the scope of this invention are shown in Table 1. Results outside of the scope of this invention are shown in Table 2. Also, in Table 3, the results of No. 2 from Table 1 and No. 1 from Table 2 are shown. Furthermore, the resin compounds in the tables are those later described in the application examples. Regarding the testing methods, a dumbbell No. 1 in accordance with JIS-K-6301 was used and it was measured at 23 °C. In the tables, the values are in %, and the values in parenthesis represent the holding rate shown in % of the values for the respective number of months based on the value when the number of months was 0 (zero). (The remainder of the page is intentionally left blank.)

Table 1. (Results within the scope of this invention)

			1	2	3	4	5
Resin Compound			A	A	A	A	B
Styrene Content (%)			25	30	35	40	35
Deterioration of Tensile Expansion (%)	No. of Months Passed	0	62	61 (100)	58	56	54
		3	60	62 (102)	56	53	52
		6	61	60 (98)	55	50	53
		9	59	58 (95)	54	43	52
		12	60	58 (95)	55	41	50
			6	7	8		
Resin Compound			E	C	Epoxy-Acrylate (Dick-Lite E-1150)		
Styrene Content (%)			35	35	35		
Change in Tensile Expansion (%)	No. of Months Passed	0	120	185	48		
		3	118	170	46		
		6	121	165	47		
		9	116	168	45		
		12	117	163	42		

Table 2. (Results outside of the scope of this invention)

			1	2	3	4
Resin Compound			A	A	E	C
Styrene Content (%)			45	50	45	45
Change in Tensile Expansion	No. of Months Passed	0	52 (100)	48	120	185
		3	43 (83)	25	96	114
		6	32 (62)	15	66	53



(%)		9	20 (44)	8	36	26
		12	14 (27)	6	14	11

When the monomer for bridging becomes less than 25%, the viscosity increases, and this poses a problem in practical applications because the resin penetration of the reinforcement material decreases.

The preferred viscosity of the polymerizing monomer-bridging heat-hardening resin compound in this invention is 0.5 ~ 20 Poise, more preferably 1.0 ~ 5 Poise. When viscosity is higher, it is hard to mix. On the other hand, if it is low, the mixed ingredients tend to separate easily.

The most important point in this invention is the combination of the hardening resin with flexibility within a specific range of fiber reinforcement materials. In case of the hardening resin alone, even if its own expansion is great, bendability at low temperatures and the crack follow-up deteriorate significantly. This is considered to be caused by the large temperature dependency of heat hardened resin, and its becoming harder as the temperature drops. On the other hand, if a fiber reinforcement material is used in combination and when a concentrated load such as zero span tension is received, because of the fiber being present, crack follow-up as well as bendability at low temperatures are improved.

Regarding the crack follow-up, if a movable concrete part is used, it must be able to satisfy the cracking width tolerances set forth by the Civil Engineering Society and by the Construction Society, which are 0.2 mm and 0.3 mm, respectively. Furthermore, the material will be repeatedly exposed to vibration and heat and cold on-site where it is used. Therefore, considering the safety margin, a follow-up that is several times higher than that noted above will be required.

The fiber reinforcement materials used in this invention are organic fibers, carbon fibers, metallic fibers, ceramic fibers, or combinations of those. The examples are glass fiber, amid, aramid, vinylon, polyester, phenol. When considering the ease of processing and economic efficiency, glass fiber or organic fibers are preferable.

Also, the fiber may have a flat texture, raised texture, non-woven texture, matted texture, etc., however, the matted texture is preferable due to the processing method and for maintaining thickness. Also, it is possible to cut up glass rope into 20 ~ 100 mm pieces and to use the chopped strands.

The amount of the fiber reinforcement material used in this invention is 2 ~ 25 weight %, or preferably 5 ~ 20 weight %. The effects of the amount of fiber reinforcement material mixed in when the polymerizing monomer-bridging unsaturated polyester resin compound is used, are shown in Figures 4 and 5. Low temperature bendability and the fit to the part to be covered deteriorate, when the amount of fiber reinforcement material is 25% or higher, or when it is 2% or lower.

Well known methods may be used to manufacture the fiber reinforced plastic sheet of this invention. The most popular method is the one where the sheet is continuously produced while filling the mixture of the polymerizing monomer-bridging heat-hardening resin compound and the fiber reinforcement materials that are associated with this invention between the layers of two films. The films are removed after production. This is the method used for producing FRP corrugated sheet, flat sheet, etc. Also, it is possible to produce a one-piece product, where the films are applied on one or both sides of the sheet of this invention. The films that may be used are monomers or a combination of ethylene difluoride (by DuPont, ChidraFilm), nylon, polyester, polyvinylchloride, polyvinylidene chloride, vinylon, high pressure or medium pressure polyethylene, polypropylene, cellophane, ethylene acetic acid vinyl copolymer. These films may be processed on the surface with radiation such as corona irradiation or electronic ray irradiation, or processed by etching with a chemical solution, in order to improve the adhesion to the sheet of this invention.

The thickness of the sheets of this invention greatly affects the ease of processing (formability), low temperature flexibility, the crack follow-up, as does the amount of fiber reinforcement material mixed in. If the thickness is to be low, a thickness of 0.4 ~ 1.8 mm is appropriate. If it is less than this range, the crack follow-up decreases. If it is thicker than this range, the ease of processing and flexibility at low temperatures may not be sufficient.

The fiber reinforced plastic sheet so manufactured is used by joining it with concrete and other materials. The available joining methods are, e.g., mechanical joining with rivets, a method using two-sided adhesive tape, a method using various types of adhesives. When using adhesives, it is preferable to use an adhesive with the smaller temperature dependency. Some of the examples are urethane, epoxy, unsaturated polyester resin.

When used in such manner, the sheet of this invention has a smaller variation of flexibility (tensile expansion rate) over time, and superior fit to the part to be covered, even after a prolonged period of time. Since it is reinforced with fiber reinforcement material, it shows superior durability

against loads from outside due to tension, bend, shear, etc., when used as a lining material for concrete, for example. In particular, the effect is great when loads are added repeatedly.

Such sheet of this invention is suitable as water proofing material for roofing in cold locations, floor lining material, and lining material for various towers and tanks. It is also suitable as lining materials for pipes for which major change occurs over time. In such cases, sheet using a film of fluoride resin, vinylchloride or vinylidene chloride on at least on one side are suitable as corrosion resistant lining material.

This invention provides structural materials lined with such sheet as well. However, it also provides lamination material where the sheet may be used not only on the surface but also with other materials in lamination.

### Application Examples

The application examples of this invention are explained below.

First, the polymerizing monomer-bridging heat-hardening resin compound is prepared as follows:

Unsaturated polyester is synthesized by heating and condensing 3 mols of diethylene glycol, 7 mols of triethylene glycol, 3 mols of maleic acid anhydride, 7 mols of orthophthalic acid, 50 ppm of tolhydroxinon at 200 ~ 20°C, and when the acid value reaches 28, the reaction is completed. 20 weight parts of styrene monomer is agitated and dissolved in 70 weight parts of the said resin to produce the polymerizing monomer-bridging heat-hardening unsaturated polyester resin compound A.

The polymerizing monomer-bridging heat-hardening unsaturated polyester resin compounds B ~ E for the application examples and the resins F and G for the comparison examples were similarly synthesized. The details of the compositions are shown in Table 3.

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Table 3. (Composition and properties of the resin compounds)

	For Application Examples	For Comparison Examples
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Resin Compounds		A	B	C	D	E	F	G
Alcohol Ingredient	DEG	3			3.5	0.86	9	
	TEG	7				1.74		
	EG		1					
	PG		1					3
	PPG400		3					
	XPG			9.8				
Unsaturated and Saturated Dibasic Acid	OPA	7	4		0.8	2.21		2
	AA			9.0	0.5		2	
	TPA				1.2			
	IPA						4	
	FA			0.4				
	MA	3	1	0.4	1.0	0.35	3	1
Styrene Content (%)		30	30	36	35	30	30	30
Double Bond Titer (Content of the Acid Above (%))		851 (11.5)	1945 (5.0)	2592 (3.5)	780 (11.4)	1907 (4.8)	644 (13.3)	568 (15.7)

In the table, PEG represents diethylene glycol, TEG represents triethylene glycol, EG represents ethylene glycol, PG represents propylene glycol, PPG400 represents polypropylene glycol, NPG represents neopentyl glycol, OPA represents orthophthalic acid, AA represents adipic acid, TPA represents terephthalic acid, IPA represents isophthalic acid, FA represents fumaric acid, and MA represents maleic acid anhydride.

#### Application Example 1.

Naphthenic acid cobalt 0.4% was added to the polymerized monomer-bridging heat-hardening unsaturated polyester resin compound B and agitated. Then MEKPO (methyl ethyl ketone peroxide) was further added and agitated to produce a resin compound.

This resin compound was spread onto a 30  $\mu$  polyester film, onto which the chopped glass fibers, 5 cm in length, in a ratio of 15% to the resin solids, was spread, which was further lined over the top by a polyester film similar to the one noted above. Then, altogether, this was placed onto a glass sheet, pressed with a grooved steel roll to sufficiently press the resin compound into the glass fiber. Next, this was clamped between two glass sheets using a spacer and left undisturbed for 2 hours. A 1 mm thick flat sheet was obtained upon removal. The resin in the flat sheet that was obtained in this manner was hardened, however, this flat sheet was further cured in an oven for 3 hours at 80°C.

From this flat sheet, a JIS-K-6301 No. 1 dumbbell was collected to measure tensile strength and the tensile expansion rate. The results were 150 kg/cm<sup>2</sup> and 15%, respectively.

Furthermore, in order to evaluate low temperature flexibility, a sample strip of 150 mm length x 30 mm width x 1 mm thickness was prepared. The strip was left standing at -10°C for 4 hours, then tested for bending resistance using a JIS-K-5400 bending test apparatus. As a result, there was no breakage up to a diameter of 4 mm.

Next, as an application test, a test for the fit to the part to be covered was performed. The test method was in compliance with the bending test for the crack follow-up testing method according to "the test methods for resin materials used in concrete repairs" set forth by the Hanshin Highway Agency. That is, for the concrete test method, the molded frame in accordance with JIS A 1132 and the concrete blends shown in Table 4 that had been preserved for 1 month were used.

Table 4.

Blend Name	W/C (%)	Target Slump	Target Air Vol. %	S/A (%)	Unit Water Vol. (kg/m <sup>2</sup> )	Absolute Volume (liter/m <sup>3</sup> )		
						Cement	Fine frame material	Rough frame material
Blend A (Regular Cement)	50	8 ~ 10	4 ± 1	43.0	165			
						104	297	394

Table 4. (Continued)

Absolute Volume (liter/m <sup>3</sup> )			Mixing Agent, Bozoris No. 70 (303A)
Cement	Fine frame material	Rough frame material	
330	772	1060	Cx 0.25% (0.73A)

The surface was finish by polishing the lining surface of the sheet with #30 sandpaper. In addition, the application method of the FRP layer was to install the FRP directly onto the concrete. In reality, because it is sheet material, it is practical to use an adhesive. However, in order to eliminate the effects of the adhesive, we adopted the direct method.

Furthermore, a three-point bending load test as shown in Figure 6 was performed. That is, the test

sample 2 lined with the sheet 1 of this application example was placed on the support stand 4 and supported at point 3 in the center of its lower surface. Then, both ends of the upper surface were pressed at points 6 and 7 with a load digit 5. In the figure, 8 represents the load cell and 9 represents the displacement meter.

With this equipment, the cracks on the concrete surface and the amount of the sample flexibility at the time when the break occurred in the sheet were measured. The tests were conducted at 20°C and -10°C.

The test results are shown in Tables 5 and 6.

In addition, the results of the tests for sample thickness, crack follow-up, and bendability performed similarly as above using the specifications noted in Tables 7 and 8, are shown in Tables 7 and 8.

#### Comparison Examples 1 and 2

The results of the tests for the sample thickness, the crack follow-up, and the bendability performed similarly as above using the specifications noted in Tables 7 and 8, are shown in Tables 7 and 8.

#### Application Example 2.

The results of the bending resistance test (measured at -10°C) of the test samples which were prepared as in Application Example 1, except for changing the fiber content percentage by using the polymerizing monomer-bridging heat-hardening unsaturated polyester resin compound A obtained above, are shown in Figure 4. The measurement results for the crack width and the tensile expansion rate are shown in Figure 5. The test methods were the same as in Application Example 1.

#### Application Examples 3 ~ 14, Comparison Examples 3 ~ 8

As in Application Example 1, the test samples were prepared according to the specifications

shown in Table 5. The results of the test are shown in Table 5.

Further, in the table, the "direct" method indicates the same installation method as in Application 1, and "adhesive" indicates that the sheet was applied using an adhesive. In this application method, after finishing the surface of the concrete sample, sheet material of 150 mm length x 500 mm width x 1 mm thickness was pressed at 0.4 kg/m<sup>2</sup> and applied using an adhesive (2 liquid mixed urethane resins, main material, Bandex JP-303 made by Dainippon Ink & Chemicals, Inc.). The follow-up test was conducted after the adhesive had hardened.

In addition, for some of the application examples and the comparison examples shown in Table 5, the bending resistance test was performed as in Application Example 1. The results are shown in Table 6.

#### Application Example 15.

Flat sheet, approximately 0.8 mm thick, was continuously produced, with the resin prepared by mixing the polymerized monomer-bridging heat-hardening unsaturated polyester resin compound B premixed with naphthenic acid cobalt 4% with a resin mixed with 1.0% MEKPO, and Polyester Super Bond (LDA-1012 (G9 120 g/m<sup>2</sup> mark, made by Japan Lutrville, K.K.) as the reinforcer. The production machine was a wave/flat continuous production machine made by Moriyama Works, K.K. The sheet was produced at a pulling speed of 2 m/min., and a hardening tank temperature of 120 ~ 80°C. The flat sheet produced in such a manner was subjected to the same tests as in Application Example 1. The results are shown in Tables 5 and 6. (The remainder of the page intentionally left blank.)

Table 5. (Relationship between sheet composition and crack follow-up test result)

		Composition of the Fiber Reinforced Plastic Sheet					Crack Width		Flexure (mm)	
		Resin Com-pound	Glass Chopp-ed (%)	Non-w oven Textile (%)	Thick-ness (mm)	Installa-tion Method	20°C	-10°C	20°C	-10°C
Appli-cation Exam-ples	1	B	15		1.0	Direct	2.7	1.8	10.2	7.5
	3	A	8		1.0	Direct	1.8	1.1	6.3	4.5
	4	A	15		1.0	Direct	2.3	1.3	8.4	6.3
	5	A	19		1.0	Direct	1.9	1.2	7.6	5.7
	6	A	25		1.0	Direct	1.6	0.9	6.2	4.6

	7	C		7	1.0	Direct	2.2		9.8	
	8	C		14	1.2	Direct	3.2	2.1	11.6	8.7
	9	C		21	1.3	Direct	2.7		9.7	
	10	C		25	1.2	Direct	1.6	1.2	7.4	5.6
	11	D	15		1.0	Direct		1.2		5.9
	12	E	15		1.0	Direct		1.9		7.2
	13	B	15		1.0	Adhesive	2.9	2.0	10.6	7.9
	14	C	15		1.0	Adhesive	3.4	2.3	12.5	9.2
	15	B		11	1.0	Adhesive	3.2	2.4	12.1	8.8
Comparison Examples	3	A	0		1.0	Direct	0.05	0.02	0.4	0.2
	4	C		0	1.0	Direct	0.08	0.04	1.5	0.4
	5	F	15		1.0	Direct	0.5	0.05	0.6	0.3
	6	C	15		1.0	Direct	0.3	0.02	0.4	0.1
	7	F		15	1.2	Direct	0.8	0.1	0.9	0.5
	8	B"	15		1.0	Direct	0.6	0.07	0.8	0.4

In the table, B" represents a styrene amount of 45 weight %.

Table 6. (Relationship between sheet composition and bending test results)

	Composition of the Fiber Reinforced Plastic Sheet			Bending Test
		Resin Compound	Fiber Content (%)	Minimum Diameter with No Break
Application Examples	4	A	Glass 15	8
	1	B	Glass 15	4
	8	C	Non-woven Textile 14	2
	11	D	Glass 15	10
	12	E	Glass 15	4
	15	B	Non-woven Textile 11	2
Comparison	5	F	Glass 15	More than 20
	6	G	Glass 15	More than 20

Table 7. (Relationship between sheet thickness and follow-up test of the crack width)

		Composition of the Fiber Reinforced Plastic Sheet					Crack Width		Flexure (mm)	
		Resin Compound	Glass Chopped (%)	Non-woven Textile (%)	Thickness (mm)	Installation Method	20°C	-10°C	20°C	-10°C
Appl. Ex. 1, Test #	1	B	15		0.5	Direct	2.1	1.3	6.5	5.4
	2	B	15		0.8	Direct	2.5	1.6	8.7	7.1
	3	B	15		1.0	Direct	2.7	1.8	10.2	7.5
	4	B	15		1.6	Direct	2.6	1.7	9.4	6.8
Comparison	1	B	15		0.2	Direct	0.5	0.1	1.4	0.3
	2	B	15		2.0	Direct	1.8	1.1	7.6	5.4



Table 8. (Relationship between sheet thickness and bending test results)

	Composition of the Fiber Reinforced Plastic Sheet			Thickness (mm)	Bending Test
		Resin Compound	Fiber Content (%)		Minimum Diameter With No Break
Appl. Ex. 1, Test 1	1	B	Glass 15	0.5	3.0 mm
	2	B	Glass 15	0.8	3.5 mm
	3	B	Glass 15	1.0	4.0 mm
	4	B	Glass 15	1.6	6.0 mm
Comparison	1	B	Glass 15	1.2	2.5 mm
	2	B	Glass 15	2.0	16 mm

### Effects of the Invention

In accordance with this invention, fiber reinforced plastic sheet which is a formed and hardened material from a compound consisting of polymerizing monomer-bridging heat-hardening resin compound and fiber reinforcer does not need to be hardened at the time of on-site installation and it is easy to handle. And it has superior extension over time as well as superior flexibility at low temperatures. In particular, it has superior fit to the part to be covered during winter.

Also, civil construction materials for which such sheet is used as the reinforcer, show improved prevention of cracking and improved resistance against bending. This would result in reinforcement of civil constructions for which it has been used.

### 4. BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graph showing the relationship between the double bond titer of unsaturated polyester and the tensile expansion rate. Figure 2 is a graph showing the double bond titer of unsaturated polyester and the inner diameter at the time of break. Figure 3 is a graph showing the change in tensile expansion holding rate over time for hardened unsaturated polyester resin. Figure 4 is a graph showing the relationship between the percentage of the fiber content and the inner diameter at the time of break in the bending test. Figure 5 is a graph showing the relationship between the percentage of fiber content and crack width. Figure 6 is a drawing of the device measuring the crack width in the follow-up test of moveable parts.

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Figure 1.

X-axis: Double bond titer of unsaturated polyester

Y-axis: Tensile expansion rate (%)

Figure 2.

X-axis: Double bond titer of unsaturated polyester

Y-axis: Inner diameter at the time of break (mm)

Figure 3.

X-axis: Time (No. of months)

Y-axis: Tensile extension holding rate of the hardened resin (%)

Styrene 90%

Styrene 45%

Figure 4.

X-axis: Fiber content (weight %)

Y-axis: Inner diameter at the time of break (mm)

Break

Break

Figure 5.

X-axis: Fiber content (weight %)

Y-axis (left): Crack width (mm)

Y-axis (right): Tensile extension rate (%)

Tensile extension rate

Crack width

Figure 6.